Particular features of crystallization and chemical nature of diphosphates in the system $MnSO_4 – CoSO_4 – K_4P_2O_7 – H_2O$

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Individual cobalt(II) and manganese(II) diphosphates are used as a basis of various modern materials such as catalysts in organic synthesis, corrosion-resistant coatings, components of lubricating fluids etc. It is perspective to synthesize solid solution based on Co(II) and Mn(II) diphosphates with a variable Co : Mn ratio on purpose to improve physico-chemical and production characteristics of the materials. The aim of this work was to find out the conditions of synthesis of solid solutions based on hydrated manganese(II) and cobalt(II) diphosphates and to determine their chemical nature.

$Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ and $Co_{2-x}Mn_xP_2O_7 \cdot 6H_2O$ diphosphates were synthesized by interaction of the mixture of manganese(II) and cobalt(II) sulfates in the water solutions with potassium diphosphate solution, taken in a certain ratio. The most significant parameters of their synthesis has been established that appeared to be the atomic ratio of components in initial solutions $n = P_2O_7^{4-}: \Sigma Me^{2+} = 0.25$; K = Mn : Co = 9,00÷0,02; concentration of solutions equal to 0.1 mole/l; duration of contact between a solid phase and a parent solution enough to achieve the equilibrium; temperature of 293─298 K. Using a complex of chemical and physico-chemical methods of research it was established that $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ and $Co_{2-x}Mn_xP_2O_7 \cdot 6H_2O$ present solid solutions of substitution with limited solubility on the basis of diphosphate-matrixes of $Mn_2P_2O_7 \cdot 5H_2O$ and $Co_2P_2O_7 \cdot 6H_2O$, which have different structure. The limits of homogeneity of solid solutions was defined as $0 < x \leq 0,83$ and $0 < x \leq 0,23$, respectively.

By X-ray diffraction method it was established that $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ solid solutions crystallize in orthorhombic system and they were structural analogs of $Mn_2P_2O_7 \cdot 5H_2O$. $Co_{2-x}Mn_xP_2O_7 \cdot 6H_2O$ solid solutions crystallize in monoclinic system and they are structural analogs of $Co_2P_2O_7 \cdot 6H_2O$. Parameters and the volume of primary cell of the synthesized diphosphates crystalline lattice together with correlation between their values and cationic composition of diphosphates were determined.

Detailed analysis of the IR spectra of synthesized diphosphates allowed us to estimate the cation nature effect on the energy of hydrogen bonds which is realized in the structure of diphosphates. For example, the values of H-bonds energy in $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ vary depending on the composition of diphosphates within 9.5─40.8 kJ/mole. With the increase in cobalt(II) content in diphosphates the energy of H-bonds increases, causing an increase in the strength of the whole system of H-bonds at the transition from $Mn_2P_2O_7 \cdot 5H_2O$ to $Mn_{1,17}Co_{0,83}P_2O_7 \cdot 5H_2O$. The influence of the cation nature on diphosphate anion was appreciated. It was displayed in the change in the angle of P–O–P bridge bond. For example, the Δ values (where $\Delta = [\nu_{as} – \nu_s (POP)] : [\nu_{as} + \nu_s (POP)]$) for $Co_2P_2O_7 \cdot 6H_2O$, $Co_{1,80}Mn_{0,20}P_2O_7 \cdot 6H_2O$ and $Co_{1,77}Mn_{0,23}P_2O_7 \cdot 6H_2O$ are 10.94, 11.02 and 11.08 %. These changes in the Δ value characterize the gradual increase in the P–O–P bond angle and in the symmetry of unsymmetrical $P_2O_7^{4-}$ anions.

Thus, for the first time the hydrated diphosphates of $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$ ($0<x\leq0,83$) and $Co_{2-x}Mn_xP_2O_7 \cdot 6H_2O$ ($0<x\leq0,23$) composition were synthesized by the interaction in the system $CoSO_4 – MnSO_4 – K_4P_2O_7 – H_2O$. They present solid solutions of substitution with the limited solubility, which are formed owing to substitutability of isomorphic Mn(II) and Co(II) cations in the structures of $Mn_2P_2O_7 \cdot 5H_2O$ and $Co_2P_2O_7 \cdot 6H_2O$ diphosphate-matrixes. Peculiarities of diphosphates crystalline structure and their possible effect on physical and chemical properties of substituted diphosphates are discussed in the report.